INTRODUCTION OF NEW SUBSTITUENTS INTO SOME AROMATIC CATIONS

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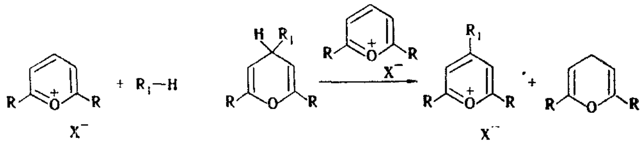
UDC 547.814'818.9'751:543.422.4

Diverse substituents in the 2- and 6-positions of pyrylium and selenapyrylium salts do not have a substantial effect on the yields in the pyrylation of dimethylaniline and 1-methylindole. The cyclopropenylation and tripylation of these compounds under conditions similar to those in the pyrylation reaction were studied; this study makes it possible to compare these three reactions.

There are an extremely large number of methods for the introduction of substituents into the ring of pyrylium salts and other heteroaromatic cations (for example, see [1]). The pyrylation reaction [2, 3] opens up broad possibilities for transformations of this sort. We have investigated this reaction in the case of the reaction of some 2,6-di(alkyl, aryl)-substituted pyrylium salts with 1-methylindole and dimethylaniline. It was found that the reaction is general in character and makes it possible to widely vary the substituents in the 2- and 6-positions of the pyrylium cations. The reaction proceeds through the intermediate formation of a 4-substituted 4H-pyran with subsequent dehydrogenation by the starting pyrylium salt [2] via the scheme



A comparison of the yields of final products (see Table 1) shows that the substituents of the starting pyrylium salt do not have a substantial effect on the reaction, although dimethylaniline is pyrylated to a somewhat lesser extent than methylindole when there are electron-donor substituents in the aromatic cation. We were unable to isolate 2,6-dimethyl-4-(p-dimethylaminophenyl)pyrylium perchlorate, probably because of the formation of a mixture of this salt with its diperchlorate (salt formation at the dimethylamino group). This was indirectly confirmed by the fact that the diperchlorate of the 2,6-di-tert-butyl-4-(p-dimethylaminophenyl)pyrylium salt was identified in the recrystallization of it from acetic acid in the presence of $HClO_4$. 2,6-Diphenylthiapyrylium perchlorate similarly undergoes thiapyrylation [4]. We ascertained that 2,6-diphenylselenapyrylium perchlorate also readily reacts with 1-methylindole and dimethylaniline to give selenapyrylium salts when mixtures of the reagents are heated slightly (see Table 1).

Similar results were obtained for nonbenzoid aromatic systems – cyclopropenylium and tropylium salts. The reaction of the triphenylcyclopropenylium cation with aromatic compounds was described in [5]. However, the tetrasubstituted cyclopropenes obtained could not be converted to new cyclopropenylium salts. It might be assumed that the use of the disubstituted cyclopropenylium cation in this reaction would lead to trisubstituted cyclopropenylium salts with a new substituent corresponding to the nucleophile used. Excess starting cyclopropenylium ion (in which case the reaction proceeds in one step) or even trityl perchlorate, which reacts with the resulting cyclopropene, may serve as hydride-ion acceptors in this case. In fact, reaction of dimethylaniline with diphenylcyclopropenylium perchlorate in acetonitrile gives 1,2-di-

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TABLE 1. Characteristics of the Compounds Obtained

Compound (-pyrylium perchlorate)	mp, °C	Empirical formula	Found, %					Calc., %					IR spectrum of pyrylium ring[d]			Yield, %
			C	H	Cl	N	Z	C	H	Cl	N	Z	8a	8b	19b	
2,6-Dimethyl-4-(1-methyl-3-indolyl)	262	$C_{16}H_{16}ClNO_5$	56,8	4,9	10,1	3,9	—	56,9	4,7	10,5	3,8	—	1670 m	1570 s	1445 inf	84
2,6-Di-tert-butyl-4-(1-methyl-3-indolyl)	286	$C_{22}H_{28}ClNO_5$	62,7	6,6	8,5	3,3	—	62,6	6,6	8,4	3,3	—	1650 s	1570 s	1430 s	92
2,6-Di-tert-butyl-4-(p-dimethylaminophenyl)	202	$C_{21}H_{30}ClNO_5$	61,0	7,4	8.7	3,6	—	61,2	7,3	8,6	3,4	—	1655 s	1555 inf	1430 s	65
2,6-Di(p-bromophenyl)-4-(p-methyl-3-indolyl)	360	$C_{25}H_{20}Br_2ClNO_5$	49,4	3,3	5,9	2,1	26,4[a]	49,2	3,3	5,8	2,3	26,2	1650 s	1550 s	1410 w	85
2,6-Di(p-bromophenyl)-4-(p-dimethylaminophenyl)	316	$C_{26}H_{18}Br_2ClNO_5$	50,5	2,8	5,6	2,4	25,7[a]	50,4	2,9	5,7	2,3	25,8	1660 m	1540 m	1415 s	85
2,6-Di(p-methoxyphenyl)-4-(1-methyl-3-indolyl)	258	$C_{28}H_{24}ClNO_7$	64,1	4,5	6,7	2,8	—	64,4	4,6	6,8	2,7	—	1630 m	1545 s	1415 m	85
2,6-Di(p-methoxyphenyl)-4-(p-dimethylaminophenyl)	312	$C_{27}H_{26}ClNO_7$	63,1	5,3	6,6	2,8	—	63,3	5,1	6,9	2,7	—	1630 m	—	1420 m	55
2,6-Di(m-hydroxyphenyl)-4-(1-methyl-3-indolyl)	304	$C_{26}H_{20}ClNO_7$	63,4	4,4	7,0	2,7	—	63,2	4,1	7,2	2,8	—	1635 s	1545 s	1415 m	98
2,6-Di(m-hydroxyphenyl)-4-(p-dimethylaminophenyl)	370	$C_{25}H_{22}ClNO_7$	62,1	4,8	7,5	2,9	—	62,2	4,6	7,3	2,9	—	1650 m	1555 inf	1425 s	84
2,6-Di(α-thienyl)-4-(1-methyl-3-indolyl)	292	$C_{22}H_{16}ClNO_5S_2$	55,9	3,5	7,6	2,8	13,4[b]	55,8	3,4	7,5	3,0	13,5	1640 s	1560 s	1425 s	95
2,6-Di(α-thienyl)-4-(p-dimethylaminophenyl)	308	$C_{21}H_{18}ClNO_5S_2$	54,3	4,0	7,5	3,1	13,7[b]	54,4	3,9	7,7	3,0	13,8	1645 s	1545 s	1420 s	95
2,6-Diphenyl-4-(1-methyl-3-indolyl)selena	247	$C_{26}H_{20}ClNO_4Se$	59,6	3,6	6,5	2,5	15,2[c]	59,5	3,8	6,8	2,7	15,1	1640 s	1545 s	1420 s	70
2,6-Diphenyl-4-(p-dimethylaminophenyl)selena	253	$C_{25}H_{22}ClNO_4Se$	58,4	4,1	6,7	2,6	15,6[c]	58,3	4,3	6,9	2,8	15,4	1630 m	1570 m	1425 m	65

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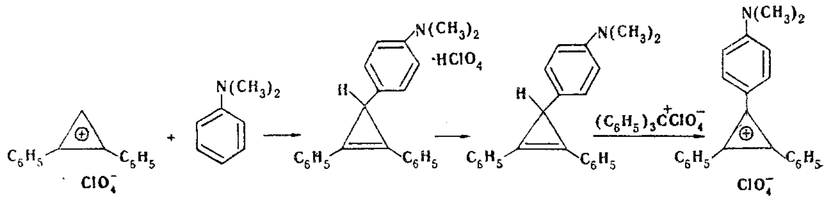
[a] Z = Br. [b] Z = S. [c] Z = Se. [d] The characteristic frequencies were numbered in accordance with the Wilson system.

phenyl-3-(p-dimethylaminophenyl)cyclopropene. The latter can be converted to a cyclopropenylium perchlorate by means of triphenylmethyl perchlorate.



Diphenylcyclopropenylium perchlorate reacts with 1-methylindole to give a mixture of indolyl-substituted cyclopropenylium salts and cyclopropene. The latter is converted to the cation by splitting out of a hydride ion by the action of trityl perchlorate. It is clear that the splitting out of a hydride ion from the intermediate indolylcyclopropene in the cyclopropenylation of indole is realized by excess starting diphenylcyclopropenylium ion because of the greater electron-donor character of indole as compared with dimethylaniline. At the same time, almost complete tropylation of indole occurs in the reaction of tripylium perchlorate with 1-methylindole. This indicates the greater electrophilic character of the tropylium cation as compared with the cyclopropenylium cation. Thus, the electrophilicity decreases in the following order: heteroaromatic cations (pyrylium, thiapyrylium, and selenapyrylium salts), tropylium cation, and cyclopropenylium cation.

1,2-Diphenyl-3-(1-methyl-3-indolyl)cyclopropenylium perchlorate is also obtained by reaction of diphenylcyclopropenone with 1-methylindole in the presence of $POCl_3$.

The intense bands at 1600-1630 and 1400-1500 cm^{-1} and other bands (according to [6]) in the IR spectra of heteroaromatic cations confirm the structure of the heterocycles (Table 1). The indolyl- and p-dimethylaminophenylcyclopropenylium perchlorates are characterized by IR bands at 3130-3145 and 1410-1430 cm^{-1} (according to [7, 8]). A number of bands at 1610, 1515, 1450, and 1100 cm^{-1} confirm the presence of aromatic and indole substituents and the ClO_4^- anion. A comparison of the IR spectra of unsubstituted [9] and indolyl-substituted tropylium cations makes it possible to isolate the most characteristic bands peculiar to these compounds (650, 980, 1040, 1500, and 3900 cm^{-1}). In contrast to the unsubstituted tropylium ion, the last two bands show up weakly in the spectrum of the indolyl-substituted tropylium perchlorate.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The pyrylium salts were obtained by the methods in [10, 11], while the diphenylcyclopropenylium and tropylium perchlorates were obtained by the methods in [12, 13], respectively.

Pyrylation of Aromatic and Heterocyclic Compounds by 2,6-Disubstituted Pyrylium Salts. A mixture of 0.01 mole of the pyrylium salt and 0.075 mole of dimethylaniline or 1-methylindole in 10-15 ml of dry dimethylformamide (DMFA) was refluxed for 30 min. It was then cooled, and the precipitated crystals were separated, washed with ether, dried, and recrystallized from acetic acid or nitromethane (see Table 1).

1,2-Diphenyl-3-(p-dimethylaminophenyl)cyclopropenylium Perchlorate. A mixture of 2.9 g (0.01 mole) of diphenylcyclopropenylium perchlorate and 1.2 g (0.01 mole) of dimethylaniline in 15 ml of acetonitrile was refluxed for 30 min. Ether (100 ml) was added, and the mixture was allowed to stand overnight. The precipitated crystals were separated, washed with ether, and dried to give 3.0 g (73%) of a product with mp 180° (nitromethane–ethyl acetate). Found, %: 66.9; H 5.4; Cl 8.4; N 3.3. $C_{23}H_{22}ClNO_4$. Calculated, %: C 67.1; H 5.3; Cl 8.6; N 3.4.

1,2-Diphenyl-3-(p-dimethylaminophenyl)cyclopropene. The cyclopropenylium perchlorate obtained above was treated in alcohol with a small amount of ammonia, after which the mixture was diluted with water, and the final product was isolated. The yield of product with mp 115° (from alcohol) was quantitative. Found, %: C 88.6; H 6.8; N 4.4. $C_{23}H_{21}N$. Calculated, %: C 88.7; H 6.7; N 4.5.

1,2-Diphenyl-3-(p-dimethylaminophenyl)cyclopropenylium Perchlorate. A mixture of 0.62 g (0.002 mole) of 1,2-diphenyl-3-(p-dimethylaminophenyl)cyclopropene and 0.68 g (0.002 mole) of trityl perchlorate in 7 ml of glacial acetic acid was refluxed for 15 min, after which it was cooled, and the resulting crystals were separated, washed with ether, and dried to give 0.61 g (74%) of a product with mp 265° (from nitromethane). Found, %: C 67.1; H 4.9; Cl 8.5; N 3.3. $C_{23}H_{20}ClNO_4$. Calculated, %: C 67.4; H 4.9; Cl 8.6; N 3.4.

1,2-Diphenyl-3-(1-methyl-3-indolyl)cyclopropenylium Perchlorate. A solution of 0.58 g (0.002 mole) of diphenylcyclopropenylium perchlorate and 0.13 g (0.001 mole) of 1-methylindole in 10 ml of dry acetonitrile was refluxed for 30 min, after which it was diluted with 30 ml of ether, and the resulting crystals were separated, washed with ether, and dried to give 0.22 g (52%) of product. 1,2-Diphenyl-3-(1-methyl-3-indolyl)cyclopropene with mp 57° (from hexane) was isolated from the filtrate. Found, %: C 89.5; H 6.1; N 4.2. $C_{24}H_{19}N$. Calculated, %: C 89.7; H 5.9; N 4.4. The latter was converted in the usual way with trityl perchlorate to an indolyl-substituted cyclopropenylium perchlorate in 20% yield of product with mp 239° (nitromethane–ether) was 72%. Found, %: C 68.5; H 4.5; Cl 8.2. $C_{24}H_{18}ClNO_4$. Calculated, %: C 68.6; H 4.3; Cl 8.5.

1-Methyl-3-indolyltropylium Perchlorate. This compound was similarly obtained by cyclopropenylation from 1-methylindole and tropylium perchlorate. When ether was added, the final product with mp 224-225° (nitromethane–ether) was isolated in 93% yield. Found, %: C 60.4; H 5.0; Cl 11.0; N 4.5. $C_{16}H_{14}ClO_4$. Calculated, %: C 60.1; H 4.4; Cl 11.1; N 4.4.

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